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## (54) NON-AQUEOUS SECONDARY BATTERY

(57) Abstract:

**PROBLEM TO BE SOLVED:** To improve energy quantity of a lithium secondary battery, and improve the cycle lifetime thereof by forming the battery out of a positive electrode having positive electrode active material as a transition metal oxide capable of absorbing and releasing lithium, a negative electrode having negative electrode material using the compound including a silicon atom, and the non-aqueous electrolyte.

**SOLUTION:** A positive electrode having positive electrode active material LiCoO<sub>2</sub> as a transition metal oxide capable of absorbing and releasing lithium and a mixture material of acetylene black and polyvinylidene fluoride is manufactured. A negative electrode having negative electrode material of the alloy including a silicon atom and having 0.01-50  $\mu$ m of mean grain size and including at least one kind or more of alkali earth group metal, transition metal and semimetal is manufactured. Furthermore, the colorless electrolyte having a specific gravity at 1.135 and formed by dissolving ethylene carbonate in the diethyl carbonate little by little and dissolving LiBPF<sub>6</sub> and LiPPG in order is filled between the positive electrode and the negative electrode. With this structure, the discharging capacity, energy quantity and cycle lifetime are improved.

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## CLAIMS

## [Claim(s)]

[Claim 1]In a nonaqueous secondary battery which makes a component an anode which has positive active material, a negative electrode which has a negative pole material, and nonaqueous electrolyte. A nonaqueous secondary battery, wherein this positive active material is a transition metal oxide in which insertion discharge of lithium is possible and this negative pole material is a compound containing a silicon atom in which insertion discharge of lithium is possible.

[Claim 2]The nonaqueous secondary battery according to claim 1, wherein a mean grain size of this silicon compound is 0.01-50 micrometers.

[Claim 3]The nonaqueous secondary battery according to claim 1 or 2, wherein this silicon compound is an alloy.

[Claim 4]The nonaqueous secondary battery according to any one of claims 1 to 3, wherein this silicon compound is the silicon which removed metal from a metal silicide.

[Claim 5]The nonaqueous secondary battery according to any one of claims 1 to 4, wherein this silicon compound has adhered with ceramics which do not react to lithium.

[Claim 6]The nonaqueous secondary battery according to any one of claims 1 to 5, wherein this silicon compound is covered with metal at least.

[Claim 7]The nonaqueous secondary battery according to any one of claims 1 to 6, wherein this silicon compound is beforehand covered with thermoplastics.

[Claim 8]The nonaqueous secondary battery according to any one of claims 1 to 7 living carbon together 5 to 1900% by a weight ratio to this silicon compound.

[Claim 9]The nonaqueous secondary battery according to any one of claims 1 to 8 if the charge-and-discharge range of this silicon compound is expressed with  $Li_xSi$  to silicon as equivalent ratio of lithium which carries out insertion discharge, wherein  $x$  is within the limits of 4.2 or less { 0 or more }.

[Claim 10]this positive active material --  $Li_yMO_2$  (M=Co and nickel --) { Fe and } At least one sort of Mn, a compound expressed with  $y=0.1-2$ , or a compound which has the Spinel structure expressed with  $Li_xNi_2O_4$  (N=Min  $x=0-2$ ), -- the nonaqueous secondary battery according to any one of claims 1

to 2 using one soft even if small.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the long lithium secondary battery of a cycle life with a nonaqueous secondary battery, especially high capacity.

[0002]

[Description of the Prior Art] The lithium contained in positive active material is first inserted in a negative pole material, and the activity of a negative pole material is raised in the lithium secondary battery using the negative pole material which does not contain a lithium metal, and the positive active material containing lithium. This is a charge reaction and the reaction which makes a lithium ion insert in positive active material from the reverse negative pole material is a discharge reaction. Carbon is used as this type of a lithium cell negative pole material. The theoretical capacity of carbon ( $C_6$ Li) is 372 mAh/g, and further high capacity negative pole material is desired. On the other hand, the theoretical capacity of the silicon which forms lithium and an intermetallic compound surpasses 4000 mAh/g, and it is known well that it is larger than that of carbon. For example, silicon of a single crystal is indicated in JP,5-74463,A, and amorphous silicon is indicated in JP,7-29602,A. In the alloy having contained silicon, the example which contains silicon in Li-aluminum alloy is indicated by JP,63-66363,A (silicon is 19 % of the weight), said 63-174275 (silicon is 0.05 to 1.0 % of the weight), and the 63-235885 (silicon is 1 to 5 % of the weight). However, since each of such alloy patent application made lithium the subject, the compound which does not contain lithium was used for positive active material. In JP,4-109562,A, 0.05 to 1.0% of the weight of the alloy is indicated for silicon. In JP,52-226863,A, the method of mixing graphite powder with lithium and the metal in which an alloy is possible is indicated. However, it has not come to use by all being inferior in a cycle life. As a reason which is inferior in the cycle life of silicon, volume expands by that the electron conductivity is low and lithium insertion, and it is guessed that pulverization of the particles is carried out.

[Problem(s) to be Solved by the Invention] The purpose of this invention is to raise the amount of

energy of a lithium secondary battery, and to raise a cycle life.

[0004]

[Means for Solving the Problem] In a nonaqueous secondary battery made into a component, a technical problem of this invention is an anode which has positive active material, a negative electrode which has a negative pole material, and nonaqueous electrolyte this positive active material. It is a transition metal oxide containing lithium, and has solved with a nonaqueous secondary battery using a compound containing a silicon atom as this negative pole material.

[0005]

[Embodiment of the Invention] Although the mode of this invention is explained below, this invention is not limited to these.

- (1) The nonaqueous secondary battery which this positive active material is a transition metal oxide which can carry out insertion discharge of the lithium, and is characterized by using the compound containing a silicon atom as this negative pole material in the nonaqueous secondary battery which makes a component the anode which has positive active material, the negative electrode which has a negative pole material, and nonaqueous electrolyte.
- (2) The nonaqueous secondary battery whose mean grain size of the silicon compound of a paragraph (1) is 0.01-50 micrometers.
- (3) The nonaqueous secondary battery whose silicon compound of a paragraph (1) is an alloy.
- (4) The nonaqueous secondary battery whose at least one sort of metal other than silicon is alkaline-earth metals, a transition metal, and semimetal in the alloy of a paragraph (3).
- (5) The nonaqueous secondary battery whose at least one sort of a paragraph (3) or the metal of (4) is germanium, Be, Ag, aluminum, Au, Cd, Ga, In, Sb, Sn, and Zn.
- (6) The nonaqueous secondary battery which contains at least one sort chosen from Mg, Fe, nickel, Co, Ti, Mo, and W in a paragraph (5).
- (7) The nonaqueous secondary battery whose atomic ratio to silicon of the metal indicated in a paragraph (6) is 20% or less exceeding 0.
- (8) Paragraph (3) Nonaqueous secondary battery whose atomic ratio of this metal to silicon given in (7) is 5 to 90%.
- (9) Paragraph (3) Nonaqueous secondary battery produced by - (8) by the alloy of a statement calcining.
- (10) The nonaqueous secondary battery whose calcination temperature is not less than 1000 °C and 1600 °C or less in a paragraph (9).
- (11) The nonaqueous secondary battery whose cooling temperature after calcination of an alloy is above by 10 °C in a paragraph (9) or (10).
- (12) The nonaqueous secondary battery which is the silicon in which the silicon compound of the statement removed metal from the metal silicide in the paragraph (1).
- (13) The nonaqueous secondary battery whose metal silicide given in a paragraph (12) is a lithium silicide.

(14) The nonaqueous secondary battery whose lithium content of a lithium silicide given in a paragraph (13) is 100-420 atom% to silicon.

(15) The nonaqueous secondary battery which is the silicon from which lithium was removed by processing a lithium silicon ghost in the alcohol which the silicon compound of the statement dried in the paragraph (1).

(16) The ceramics to which a silicon compound given in a paragraph (1) does not react to lithium, and an adhering nonaqueous secondary battery.

(17) The nonaqueous secondary battery which is at least one sort as which ceramics given in a paragraph (16) are chosen from aluminum<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, SiC, and Si<sub>3</sub>N<sub>4</sub>.

(18) The nonaqueous secondary battery whose ceramics given in a paragraph (17) are SiO<sub>2</sub>.

(19) The nonaqueous secondary battery whose SiO<sub>2</sub> given in a paragraph (18) is SiO<sub>2</sub> of colloid.

(20) Paragraph (15) Nonaqueous secondary battery whose weight ratio of these ceramics to a silicon compound given in - (19) is 2 to 50%.

(21) Paragraph (16) Manufacturing method of the nonaqueous secondary battery with which the method of making these ceramics adhere to the silicon compound of a statement includes the process heated below not less than 300 °C to 1600 °C in - (20).

(22) The nonaqueous secondary battery with which the silicon compound given in a paragraph (1) is covered by at least one sort of metal.

(23) A manufacturing method of the nonaqueous secondary battery which is at least one sort as which the method of making it cover with the metal of a paragraph (22) is chosen from a nonelectrolytic plating method, vacuum deposition, sputtering process, a chemical-vapor-deposition method, and the metal pushing method.

(24) The nonaqueous secondary battery whose metal with which the paragraph (22) and (23) is covered is at least one sort of nickel, Cu, Ag, Co, Fe, Cr, W, Ti, Au, Pt, Pd, Sn, and Zn.

(25) The nonaqueous secondary battery whose metal with which the paragraph (22) and (23) is covered is at least one sort of nickel, Cu, and Ag.

(26) Paragraph (22) Ten or more times [ of the specific conductance of the silicon compound with which the specific conductance of the silicon compound covered with the metal of - (25) is not covered ] the nonaqueous secondary battery.

(27) Paragraph (22) Nonaqueous secondary battery whose coating volume of the metal of - (26) is 1-80 atom% to silicon.

(28) The nonaqueous secondary battery with which the silicon compound of the paragraph (1) is beforehand covered selectively by thermoplastics.

(29) A manufacturing method of the nonaqueous secondary battery whose how to cover a paragraph (28) with thermoplastics selectively beforehand is a method including the process of mixing a silicon compound to a solvent and kneading thermoplastics after the dissolution or distribution to it.

(30) The nonaqueous secondary battery which is at least one sort as which a paragraph (28) and the

Thermoplastics of (29) are chosen from polyvinylidene fluoride and polytetrafluoroethylene

(31) Paragraph (28) Nonaqueous secondary battery whose weight ratio of thermoplastics to the silicon compound of - (30) is 2 to 30%.

(32) Paragraph (38) Nonaqueous secondary battery whose coverage of the thermoplastics of - (31) is 5 to 95%.

(3) The homogeneous secondary battery with which carbon lies together 5 to 1900% by a weight ratio to the silicon compound of a paragraph (1).

(34) The nonaqueous secondary battery with which carbon fixes together 5 to 400% by a weight ratio to the silicon compound of a paragraph (1).

(36) The aqueous secondary battery a paragraph (33) and whose carbon of (34) are scaly natural graphite.

(36) The nonaqueous secondary battery whose  $x$  is within the limits of 0 to 4.2 when the charge-and-discharge range of the silicon compound of a paragraph (1) expresses with  $\text{Li}_x\text{Si}$  to silicon as an equivalent ratio of the lithium which carries out insertion discharge.

(37) The nonaqueous secondary battery whose  $\chi$  is within the limits of 0 to 3.7 when the charge-and-discharge range of the silicon compound of a paragraph (1) expresses with  $\text{Li}_x\text{Si}$ .

(33) The nonaqueous secondary battery which stopped charge of the silicon compound of a paragraph (1) in 0.1% or more of 3 hour rate current, and 10% or less of range.

(28) The aqueous secondary battery which charges twice in a vacuum (28) out of which

hours 15 minutes or more.

(40) The positive active material of a paragraph (3) is  $Li_yMO_2$  (y: M=Co and/or Ni, Fe, and Mn). Nonaqueous secondary battery using at least one sort of the material containing  $y=0.1\text{--}2$  or the material which has the Spinel structure expressed with  $Li_xN_xO_4$  ( $N=$ Mn $\geq 0.2$ ).

(41) The positive active material of a paragraph (1) is  $\text{Li}_y\text{M}_z\text{D}_{1-y}\text{O}_2$  (1) (M=Co and) At least one sort of nickel, Fe, and Mn, D=Co, nickel, Fe, Mn, aluminum, Zn, Cu, Mo, Ag, W, Ga, In, Sn, Pb, Sb, Ag, least one sort other than M in Sr, S, and P,  $y=0.1-1$ , the material containing  $z=0.5-1$ ,  $\text{O}=\text{Li}_z(\text{M}_z\text{D}_{1-y})_{1-y}\text{O}_2$  (2) (M=Mn and) The nonaqueous secondary battery using at least one sort of material which has the Spinel structure expressed with at least one sort of D=Co, nickel, Fe, aluminum, Zn, Cu, Mo, Ag, W, Ga, In, Sn, Pb, Sb, Sr, S, and P,  $z=0.2-1$ , and  $z=0-2$ .

(42) Paragraph (3) Nonaqueous secondary battery whose mean grain size of the silicon used by (39) is 0.01-50 micrometers.

(43) Paragraph (3) Nonaqueous secondary battery whose mean grain size of the silicon used by -  
(39) is 0.05-5 micrometers.

(44) The nonaqueous secondary battery which is at least one sort by which silicon of a statement is chosen as a paragraph (42) or (43) from the silicon simple substance, silicon base alloy, and silicide which can react to lithium.

(48) Paragraph (3) Nonaqueous secondary battery whose alloy given in - (11) is an alloy to which the ceramics of paragraph (16) - (21) were made to adhere.

(49) Paragraph (3) Nonaqueous secondary battery whose alloy given in - (11) is an alloy which covered the metal of paragraph (22) - (27).

(47) The nonaqueous secondary battery whose alloy given in a paragraph (48) is an alloy which covered the metal of paragraph (22) - (27).

(48) The nonaqueous secondary battery whose alloy given in a paragraph (48) is an alloy which adhered the ceramics of paragraph (16) - (21).

(49) Paragraph (3) Nonaqueous secondary battery whose alloy given in - (11) is an alloy which covered the thermoplastics of paragraph (28) - (32).

(50) The nonaqueous secondary battery which plated paragraph (22) - (27) into the material of the paragraph (48).

(51) Paragraph (46) Nonaqueous secondary battery whose material of - (48) is the material which covered the thermoplastics of paragraph (28) - (32).

(52) The nonaqueous secondary battery whose material of a paragraph (46) is the material which covered the metal of paragraph (28) paragraph (22) - (27) after covering the thermoplastics of - (32).

(53) Paragraph (3) Nonaqueous secondary battery which is the material in which the alloy of the statement made carbon of paragraph (33) - (35) live together in - (11).

(54) Paragraph (45) Nonaqueous secondary battery whose material given in - (52) is the material which made carbon of paragraph (33) - (35) live together.

(55) Paragraph (3) Nonaqueous secondary battery which uses the negative electrode of a statement for - (11) in the charge-and-discharge range of a statement at paragraph (36) - (39).

(56) Paragraph (45) Nonaqueous secondary battery which uses the material of a statement for - (54) in the charge-and-discharge range of a statement at paragraph (36) - (39)

(57) An alloy given in a negative pole material at paragraph (3) - (11), the nonaqueous secondary battery using a compound given [ as positive active material ] in a paragraph (40) or (41).

(58) The nonaqueous secondary battery using a compound given [ as the material of paragraph (42) - (54), and positive active material ] in a negative pole material a paragraph (40) or (41).

(58) Paragraph (12) Nonaqueous secondary battery whose silicon given in - (15) is the silicon to which the ceramics of paragraph (16) - (21) were made to adhere.

(60) Paragraph (12) Nonaqueous secondary battery whose silicon given in - (15) is the silicon which covered the metal of paragraph (22) - (27)

(61) The nonaqueous secondary battery whose material of a paragraph (59) is the material which covered the metal of paragraph (22) - (27).

(62) The nonaqueous secondary battery whose material of a paragraph (60) is the material to which the ceramics of paragraph (16) - (21) were made to adhere.

(63) Paragraph (12) Nonaqueous secondary battery whose silicon given in - (15) is the silicon which covered the thermoplastics of paragraph (28) - (32).

(64) The nonaqueous secondary battery which is the material which covered the metal of paragraph (22) - (27) into a material given in a paragraph (63).

(65) Paragraph (69) Nonaqueous secondary battery whose material of - (82) is the material which covered the thermoplastics of paragraph (28) - (32).

(66) The nonaqueous secondary battery whose material of a paragraph (59) is the material which covered the metal of paragraph (38) paragraph (22) - (27) after covering the thermoplastics of - (32).

(67) Paragraph (12) Nonaqueous secondary battery which is the material in which silicon of the statement made carbon of paragraph (33) - (35) live together in - (15).

(68) Paragraph (59) Nonaqueous secondary battery whose material given in - (68) is the material which made carbon of paragraph (33) - (35) live together.

(69) Paragraph (12) Nonaqueous secondary battery which uses the negative electrode of a statement for - (15) in the charge-and-discharge range of a statement at paragraph (36) - (39).

(70) Paragraph (69) Nonaqueous secondary battery which uses the material of a statement for - (89) in the charge-and-discharge range of a statement at paragraph (36) - (39).

(71) The nonaqueous secondary battery using a compound given [ as silicon given in a negative pole material at paragraph (12) - (15), and positive active material ] in a paragraph (40) or (41).

(72) The nonaqueous secondary battery using a compound given [ as the material of paragraph (58) - (68), and positive active material ] in a negative pole material a paragraph (40) or (41).

(73) Paragraph (16) Nonaqueous secondary battery which is the silicon in which the silicon compound of the statement covered the metal of paragraph (22) - (27) to - (21).

(74) Paragraph (16) Nonaqueous secondary battery whose silicon compound given in - (21) is a silicon compound which covered the thermoplastics of paragraph (28) - (32).

(75) The nonaqueous secondary battery whose material of a paragraph (73) is the material which covered the thermoplastics of paragraph (28) - (32).

(76) The nonaqueous secondary battery whose material given in a paragraph (75) is the material which covered the metal of paragraph (22) - (27).

(77) Paragraph (16) Nonaqueous secondary battery whose silicon compound given in - (21) is a silicon compound which made carbon of (33) - (35) live together

(78) Paragraph (73) Nonaqueous secondary battery whose material given in - (77) is the material which made carbon of (33) - (35) live together.

(79) Paragraph (16) Nonaqueous secondary battery which used the silicon compound of the statement for - (21) with the charging and discharging method of the statement at paragraph (36) - (39).

(80) Paragraph (73) Nonaqueous secondary battery which used the material of the statement for - (78) with the charging and discharging method of the statement at paragraph (38) - (39).

(81) The nonaqueous secondary battery using a compound given [ as a negative pole material / as the silicon compound of paragraph (16) - (21), and positive active material ] in a paragraph (40) or (41).

(82) The nonaqueous secondary battery using a compound given [ as a negative pole material / as the material of paragraph (73) - (78), and positive active material ] in a paragraph (46) or (41).

(83) Paragraph (82) Nonaqueous secondary battery which is the material to which the material of the statement made the ceramics of the statement adhere at - (27) at paragraph (16) - (21).

(84) Paragraph (22) Nonaqueous secondary battery whose material given in - (27) is the material which covered thermoplastics given in paragraph (28) - (32).

(85) The nonaqueous secondary battery which is the material in which the material of the paragraph (80) covered the thermoplastics of the statement to paragraph (28) - (32).

(86) Paragraph (22) Nonaqueous secondary battery whose material given in - (27) is the material which made carbon of paragraph (33) - (36) live together.

(87) Paragraph (83) Nonaqueous secondary battery whose material given in - (86) is the material which made carbon of paragraph (33) - (36) live together.

(88) Paragraph (22) Nonaqueous secondary battery whose material given in - (27) is the material which made carbon of paragraph (38) - (38) live together.

(89) Paragraph (22) Nonaqueous secondary battery which used the material of the statement for - (27) with the charging and discharging method of the statement at paragraph (36) - (39).

(90) Paragraph (83) Nonaqueous secondary battery which used the material of the statement for - (88) with the charging and discharging method of the statement at paragraph (36) - (39).

(91) The nonaqueous secondary battery using a compound given [ as a material given / as a negative pole material / in paragraph (22) - (27), and positive active material ] in a paragraph (46) or (41).

(92) The nonaqueous secondary battery using a compound given [ as a material given / as a negative pole material / in paragraph (81) - (86), and positive active material ] in a paragraph (40) or (43).

(93) Paragraph (28) Nonaqueous secondary battery whose material given in - (32) is the material to which the ceramics of (16) - (21) were made to adhere.

(94) Paragraph (28) Nonaqueous secondary battery whose material given in - (32) is the material which covered metal given in (22) - (27).

(95) The nonaqueous secondary battery whose material given in a paragraph (93) is the material which covered metal given in paragraph (22) - (27).

(96) Paragraph (28) Nonaqueous secondary battery whose material given in - (32) is the material which lived carbon of the statement together in paragraph (33) - (36).

(97) The nonaqueous secondary battery whose material given in a paragraph (93) is the material which lived carbon of the statement together at paragraph (33) - (36).

(98) The nonaqueous secondary battery whose material given in a paragraph (94) is the material which lived carbon of the statement together at paragraph (33) - (36).

(99) Paragraph (28) Nonaqueous secondary battery which used the material of the statement for - (32) with the charging and discharging method of the statement at paragraph (36) - (39).

(100) Paragraph (33) Nonaqueous secondary battery which used the material of the statement for - (36) with the charging and discharging method of the statement at paragraph (36) - (39).

(101) The nonaqueous secondary battery using a compound given [ as a material given / as a negative pole material / in paragraph (28) - (32), and positive active material ] in a paragraph (40) or (41).

(102) The nonaqueous secondary battery using a compound given [ as a material given / as a negative pole material / in paragraph (33) - (36), and positive active material ] in a paragraph (40) or (41).

(103) The nonaqueous secondary battery using a compound given [ as a material given / as a negative pole material / in paragraph (37) - (39), and positive active material ] in a paragraph (40) or (41).

(104) Paragraph (38) Nonaqueous secondary battery which used the material of the statement for (25) with the charging and discharging method of the statement at paragraph (36) - (39).

(105) Paragraph (42) Nonaqueous secondary battery which used the material of the statement for (44) with the charging and discharging method of the statement at paragraph (36) - (39).

[0006] On a charge collector, positive electrode mixture (or negative electrode mixture) can be painted and fabricated, and the anode (or negative electrode) used by this invention can make it. A conducting agent, a binder, a dispersing agent, a filler, an ion conducting agent and a pressure enhancement agent, and various additive agents besides positive active material (or negative pole material) can be included in positive electrode mixture (or negative electrode mixture). As for these electrodes, it is preferred that they are discoid and a sheet shaped which is supple although it may be tubular.

[0007] The composition and material of this invention are explained in full detail below. The compound containing the silicon atom which can carry out insertion discharge of the lithium used with the negative pole material of this invention means a silicon simple substance, a silicon base alloy, and a silicide. A single crystal, polycrystal, and amorphous all can be used as a silicon compound. As for the purity of a simple substance, 85 % of the weight or more is preferred, and its 95 % of the weight or more is especially preferred. Especially 99 % of the weight or more is preferred. As an impurity, Fe, aluminum, Ca, Mn, Mg, nickel, Cr, etc. are mainly contained. Those content is 0 to 0.5 % of the weight. As for the mean grain size of a " silicon compound, 0.01-50 micrometers is preferred. In particular, 0.02-30 micrometers is preferred. 0.05-5 micrometers is preferred. Being covered with the silica dioxide is known well and the surface of silicon is considered to also carry out the duty of an ion conductivity coat.

[0008] Since a silicon base alloy controls the pulverization by expansion contraction of the silicon produced when insertion discharge of the lithium is carried out or improves the conductive leaveness of silicon, it is thought that it is effective. As an alloy, an alloy with alkaline-earth metals, a transition metal, or semimetal is preferred. In particular, a dissolution nature alloy and an eutectic nature alloy are preferred. A dissolution nature alloy says the alloy which forms a solid solution. For example, the alloy of germanium is a dissolution nature alloy. Although eutectic of the eutectic nature alloy is carried out to silicon at any rate, the solid cooled and obtained says the alloy which is a mixture of

silicon and metal. Be, Ag, aluminum, Au, Cd, Ga, In, Sb, Sn, and Zn form an eutectic nature alloy. In these, the alloy of germanium, Be, Ag, aluminum, Au, Cd, Ga, In, Sb, Sn, and Zn is still more preferred. Two or more sorts of these alloys are also preferred. The alloy which contains germanium, Ag, aluminum, Cd, In, Sb, Sn, and Zn especially is preferred. As for the mixing ratio of these alloys, 5 to 90 % of the weight is preferred to silicon, in particular, 10 to 80 % of the weight is preferred. Especially 20 to 60 % of the weight is preferred. Other Mg of an eutectic nature alloy, Fe, Co, nickel, Ti, Mo, and W may also be included. As content of these metal, 0 to 20 % of the weight is preferred. The mixing ratio in particular of metal other than silicon is not limited. In this case, although electrical conductivity improves, it is preferred battery capacity and that specific conductance will be 10 or more times of silicon in front of an alloy or the specific conductance of a silicon compound in respect of service capacity, high rate characteristics, and a cycle life especially.

[0019] The calcinating method and the mechanical milling method are used as a synthetic method of an alloy. In inactive gas, with the heating rate of 5-100 °C/min, as a calcinating method, mix the metal of a raw material, move it to a crucible, carry out temperature up, and as constant temperature. Especially, preferably, it is kept especially desirable at 1300-1700 °C for 30 minutes - 5 hours for 10 minutes - 24 hours, and 1000-1800 °C cools with the above temperature falling speed by 10 °C. Cooling above by 100 °C especially is preferred. As inactive gas, it is preferred whether it is independent in gas, such as argon, nitrogen, and hydrogen, and that it mixes and uses. Annealing is preferred after cooling. As an annealing condition, within the limits of the temperature which 200 °C - some alloys do not fuse is preferred in inactive gas.

[0020] The method of grinding two or more metal until it becomes overly detailed is used, using grinders, such as a ball mill, a planetary ball mill, and a vibration mill, as a mechanical milling method. As for the inside of the cell of a mill, it is preferred to fill with inactive gas, an inert liquid object, a reducing gas, and a reducing fluid. As inactive gas, it is preferred whether it is independent in gas, such as argon, nitrogen, and hydrogen, and that it mixes and uses. Water, alcohol, etc. which ~~are used~~ are used as an inert liquid object. Ammonia, sulfurous acid gas, etc. are used as a reducing gas. As a reducing fluid, solution and the dimethylsulfoxide solution having contained sodium sulfite, sodium subsulfite, hydroxylamine, hydroquinone, etc. can be used. Especially the thing that inactive gas grinds is preferred. As for milling time, 1 hour - 48 hours are preferred.

[0021] As for the mean grain size of an alloy, 0.01-40 micrometers is preferred. 0.02-20 micrometers is preferred especially, and especially further 0.03-5 micrometers are preferred. As the grinding method, a vibration mill, a ball mill, a planetary ball mill, a jet mill, and an automatic mortar are used. As for grinding time, 1 minute - 1 hour are preferred. The method which stated the atmosphere of grinding by the paragraph of mechanical milling is used.

[0022] A silicide says the compound of silicon and metal. As a silicide, CaSi, Ca<sub>2</sub>Si<sub>2</sub>, Mg<sub>2</sub>Si, BaSi<sub>2</sub>, SrSi<sub>2</sub>, Cu<sub>2</sub>Si, FeSi<sub>2</sub>, Fe<sub>2</sub>Si<sub>2</sub>, CoSi<sub>2</sub>, nickel<sub>2</sub>Si, NiSi<sub>2</sub>, MnSi, Mn<sub>2</sub>Si<sub>2</sub>, MoSi<sub>2</sub>, CrSi<sub>2</sub>, TiSi<sub>2</sub>, Ti<sub>2</sub>Si<sub>3</sub>, Cr<sub>2</sub>Si, NbSi<sub>2</sub>, NaSi<sub>2</sub>, CeSi<sub>2</sub>, SmSi<sub>2</sub>, DySi<sub>2</sub>, ErSi<sub>2</sub>, YSi<sub>2</sub>, WSi<sub>2</sub>, W<sub>2</sub>Si<sub>3</sub>, TaSi<sub>2</sub>, Ta<sub>2</sub>Si<sub>3</sub>, TmSi<sub>2</sub>, ThSi<sub>2</sub>, YbSi<sub>2</sub>, YEr<sub>2</sub>.

$\text{YSi}_2$ ,  $\text{ErSi}$ ,  $\text{BiSi}_2$ ,  $\text{GeSi}_2$ ,  $\text{PrSi}$ ,  $\text{Y}_2\text{Si}$ ,  $\text{VSi}_2$ ,  $\text{HfSi}_2$ ,  $\text{PdSi}$ ,  $\text{PrSi}_2$ ,  $\text{HoSi}_2$ ,  $\text{EuSi}_2$ ,  $\text{LaSi}$ ,  $\text{EuSi}$ ,  $\text{ReSi}$ ,  $\text{Rhe}$ , etc. are used.

[0013] It is preferred to use the silicon which removed metal from the metal silicide as this silicon compound. When the porous thing and the fine grain condensed by a particle of 1 micrometer or less as shape of this silicon, and formed the porous aggregated particle can be raised. It is thought as a reason a cycle life will be improved if this silicon is used that pulverization is hard to be carried out. As for the metal of this metal silicide, it is preferred that they are an alkaline metal and alkaline-earth metals. Especially, it is preferred that they are Li, Ca, and Mg. In particular, Li is preferred. As for the mean grain size of this metal silicide, it is preferred that it is 0.01-300 micrometers, its 0.01-50 micrometers are more preferred, and its 0.01-10 micrometers are the most preferred. 100-420 mol% of the lithium content of this lithium silicide is desirable to silicon. In particular, 200-420 mol% is preferred. As for the method of removing an alkaline metal and alkaline-earth metals from the silicide of an alkaline metal or alkaline-earth metals, it is preferred to make it process with the solvent reacted to an alkaline metal or alkaline-earth metals. As a solvent, water and alcohols are preferred. \* \* \* in which using the alcohol which generated in the case of the lithium silicide, and were dried can control oxidation of silicon under reaction is preferred. As a grade of drying, 1000 ppm or less of residual amount of water is preferred, 200 ppm or less are preferred, and 50 ppm or less are the most preferred. As the method of deaeration and drying, carrying out bubbling with inactive gas, such as argon, is mentioned, making this alcohol return. As a kind of alcohol, methyl alcohol, ethyl alcohol, 1-propyl alcohol, 2-propyl alcohol, 1-butyl alcohol, 2-butyl alcohol, t-butyl alcohol, 1-pentyl alcohol, 2-pentyl alcohol, and 3-pentyl alcohol are preferred. In particular, 1-propyl alcohol, 2-propyl alcohol, 1-butyl alcohol, 2-butyl alcohol, and t-butyl alcohol are preferred. Removal of Ca or Mg has preferred water. It is still more desirable when a buffer for pH which is maintained at neutral vicinity is used. Especially although what is necessary is just more than the reaction equivalent as an amount of solvents, about 10 times are preferred. Although reaction temperature does not have restriction in particular, in order to advance a reaction mildly and uniformly, it is preferred that it is below a room temperature.

[0014] Washing is preferred after taking out the residual silicon powder after ending reaction by filtration or a decantation. As a penetrant remover, the above-mentioned water and alcohols are preferred. Thus, as for the metal usage of the obtained powder, it is preferred that it is 1 or less % of the weight, and it is more preferred that it is 0.1 or less % of the weight. In order to lessen metal usage, it is preferred to make grain size of the silicide of reaction time small. Specifically 0.01-300 micrometers is preferred, 0.01-50 micrometers is more preferred, and 0.01-10 micrometers is the most preferred. After grinding the powder obtained after ending reaction as other methods and making grain size small, supplying to a reactional solvent again is also preferred. It is also preferred to repeat the aforementioned grinding and a reaction if needed. Thus, it is preferred that the after-mentioned carries out metallic coating of the obtained silicon powder at the point that service capacity and a cycle life are further improvable.

[0015] It is thought that the ceramics made to adhere to a silicon compound are effective in control of the pulverization of silicon. The compound which does not react to lithium in principle as ceramics is preferred. In particular, aluminum<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, SiC, and Si<sub>3</sub>N<sub>4</sub> are preferred. As a method to which silicon and ceramics are made to adhere, although mixing, heating, vacuum evaporation, and CVD are used, concomitant use of mixing and heating is preferred especially. After carrying out dispersion mixing of the colloidal solution (colloidal silica) and silicon of aluminum<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> especially, if you heat, the lump which dissolved can be ground and the affix of silicon, aluminum<sub>2</sub>O<sub>3</sub>, or SiO<sub>2</sub> can be obtained. With in this case, the affix of aluminum<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>. The state where the surfaces, such as aluminum<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, are covered with silicon powder, if it is shut up inside lumps, such as aluminum<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, or they are covered for the surface of silicon is said. Mechanical agitation, an ultrasonic wave, and kneading can attain mixture dispersion. Although it is preferred to perform heating in 300 °C - 1600 °C in inactive gas, 500 °C - especially 1300 °C especially are still more preferred 400 °C - 1500 °C. Cooking time's 0.5 to 24 hours are preferred. As for inactive gas, argon, nitrogen, and hydrogen are raised. These mixed gas is also used. The method which was learned with a ball mill, the vibration mill, the planetary ball mill, the jet mill, the sufficient automatic mill, etc. as for pulverizing method is used. Although the environment which also stated this grinding by mechanicals milling is preferred, it is preferred to be especially carried out in inactive gas. Although the mixture ratio of the ceramics to silicon has 2 to 50% of the weight of a preferred range, 3 to 40% is especially preferred. As for the mean grain size for which it asked from electron microscope observation of silicon, 0.01-40 micrometers is preferred, 0.5-20 micrometers is preferred especially, and 1-10 micrometers is still more preferred.

[0016] As metallic coating of the silicon compound of this invention, it can attain by vacuum deposition, such as electroplating, the substitution plating method, a non-electrolytic plating method, resistance heating vacuum deposition, electron beam evaporation, and cluster ion vacuum deposition, sputtering process, and a chemical-vapor-deposition method (CVD method). In particular, vacuum deposition, such as a nonelectrolytic plating method, resistance heating vacuum deposition, electron beam evaporation, and cluster ion vacuum deposition, sputtering process, and a CVD method are preferred. The method of pushing the metal by the high-speed-shearing mill, the stamp mill, and a roll mill is used. Especially, especially a nonelectrolytic plating method is preferred. A nonelectrolytic plating method is a volume for "nonelectrolytic plating foundation and application" electroplating study groups. \*\*\*\*\* (1984) It is indicated. The reducing agent has phosphinate, phosphonate, a boron hydride ghost, aldehyde, sugars, amines, and preferred metal salt. Sodium hydrogen phosphinate and sodium hydrogen phosphonate, sodium borohydride, dimethylamine borane, formaldehyde, sucrose, dextrin, hydroxylamine, hydrazine, ascorbic acid, and a titanium chloride are preferred. It is preferred to include a pH regulator and complexing agent other than a reducing agent in plating liquid. The compound indicated above "the nonelectrolytic plating foundation and application" also about these is used. The plating solution presentation is also

described in the above-mentioned book. As for the concentration of a reducing agent, per 1000g 1 L of water are preferred. Although the pH in particular of plating liquid is not limited, 4-13 are preferred although 10  $^{\circ}\text{C}$  - 100  $^{\circ}\text{C}$  are preferred as for the temperature of liquid -- especially -- 20  $^{\circ}\text{C}$  - 95  $^{\circ}\text{C}$  -- this -- better --  $^{\circ}\text{C}$ . The activation bath which consists of a  $\text{SnCl}_2$  hydrochloric acid aqueous solution besides a plating bath, and the nucleation bath which consists of a  $\text{PdCl}_2$  hydrochloric acid aqueous solution are used, or a filtering step, a washing process, a grinding process, and a drying process are used further.

[0017] moreover -- as the gestalt of the silicon compound covered -- both powder state mass tabular, etc -- although -- it is used, if the metal covered is conductive high metal, it is [ anything ] good, but nickel, Cu, Ag, Co, Fe, Cr, W, Ti, Au, Pt, Pd, Sn, and Zn are preferred especially, nickel, Cu, Ag, Co, Fe, Cr, Au, Pt, Pd, Sn, and Zn are preferred especially, and nickel, Cu, Ag, Pd, Sn, and especially Zn are still more preferred. Although the amount of metal in particular covered does not have limitation, it is preferred to cover so that specific conductance may be 10 or more times of the specific conductance of the silicon compound which is a base. As for especially metallized coating volume, 1 to 50 % of the weight is preferred one to 80% of the weight to silicon, and especially its further 1 to 30 % of the weight is preferred.

[0018] As for the silicon compound used by this invention, being beforehand covered with the synthetic resin selectively is preferred from a viewpoint of improvement of a cycle life. It is thought that it is because the pulverization of the silicon compound accompanying lithium insertion is controlled as a reason a cycle life is improved. Although a synthetic resin is divided roughly into thermoplastic and thermosetting resin, for cycle-life improvement, thermoplastics is more preferred. As for thermoplastics, a fluorine-containing high molecular compound, imide system polymers, vinyl system polymers, acrylate system polymers, ester system polymers, polyacrylonitrile, etc. are used. Especially thermoplastics has preferred resin which cannot swell easily to an electrolysis solution. As an example, polyacrylic acid, polyacrylic acid Na, polyvinyl phenol, Polyvinyl methyl ether, polyvinyl alcohol, a polyvinyl pyrrolidone, Water-soluble polymer, such as polyacrylamide, polyhydroxy (meta) acrylate, and a styrene-maleic acid copolymer, Polyvinylchloride, polytetraFLURURORO ethylene, polyvinylidene fluoride, A fluorinatedethylene-hexafluoropropylene copolymer, a vinylidene fluoride-tetrafluromethylene-hexafluoropropylene copolymer, Polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM), Sulfonation EPDM, polyvinyl-acetal resin, a methylmethacrylate. The acrylic ester copolymer containing acrylic ester (meta), such as 2-ethylhexyl acrylate (meta), (meta) The polyvinyl ester copolymer containing vinyl ester, such as an acrylic acid ester acrylonitrile copolymer and vinyl acetate, A styrene butadiene copolymer, an acrylonitrile-butadiene copolymer, polybutadiene, neoprene rubber, fluorocarbon rubber, polyethylene oxide, polyester polyurethane resin, An emulsion (latex) or suspension, such as polyether polyurethane resin, polycarbonate polyurethane resin, polyester resin, phenol resin, and an epoxy resin, can be mentioned. Latex of a polyacrylic ester system, carboxymethyl cellulose, polytetrafluoroethylene, and polyvinylidene fluoride are mentioned especially. It can be independent, or it can mix and these compounds can be used. In

if it is a solvent which can dissolve a synthetic resin as a solvent used here, anything can be used, but in the case of polyvinylidene fluoride, N-methyl-2-pyrrolidone or dimethylformamide is preferred. After dissolving thermoplastics as an option covered beforehand by carrying out homogeneous-mixing after baking of synthetic resin powder and the silicon compound powder, the method of grinding the obtained solid is also preferred. When grinding the obtained solid, it is preferred to grind under the inert gas atmosphere of argon etc. for control of side reactions, such as oxidation of a silicon compound. Generally the directions as a binder at the time of the thermoplastics shown above constituting a negative electrode mixture layer are known. The directions as coating of this invention differ in that an active material surface is made to carry out localization of the thermoplastics to the directions as a binder using the methods of mixing with an active material, a conducting agent, etc. uniformly, and using. Although it is known conventionally that it is a direction from which a cycle life is improved by increasing the amount of the thermoplastics used as a binder, the method of the cycle nature improvement effect which the active material surface of this invention is made to cover is larger.

[0018] As amount of the synthetic resin used to a silicon compound, 2 to 30 % of the weight is preferred. In particular, 3 to 20 % of the weight is preferred. As for a synthetic resin, in this invention, being covered selectively is preferred. Although 5 to 95% of coverage is desirable, 5 to 90% is preferred especially. It defines as the rate of percentage of the area of the portion covered with the thermoplastics to the total surface area of silicon compound particles with coverage here. Since it is generally insulation, when covering thermoplastics on the silicon compound surface, it is preferred to use together the means which raises conductivity. As a means which raises conductivity, publicly known methods, such as coexistence with carbon particles, coexistence with metal particles, and concurrent use of metal plating, can be used. As for the average size of the covered particles, 0.01 micrometer ~ 40 micrometers are preferred. In particular, 0.03-5 micrometers is preferred. It is preferred to use the carrier fluid which a synthetic resin does not dissolve as carrier fluid used when mixing with a conducting agent and a binder the particles covered with the synthetic resin and preparing negative electrode mixture. For example, when it covers with polyvinylidene fluoride, the carrier fluid used at the time of negative electrode mixture preparation has preferred water. The method of the above (the grinding method or its environment) is used. It is preferred to use metalized coating together because of grant of electron conductivity.

[0020] It is preferred to mix and use a silicon compound and a carbonaceous compound in this invention. The material for which a carbonaceous material is used with a conducting agent or a negative pole material is used. As a carbonaceous material, the charge of a difficulty graphitized carbon material and a black lead system carbon material can be mentioned. Specifically, JP,62-

these compounds, a fluorine-containing high molecular compound is preferred.

Polytetrafluoroethylene and polyvinylidene fluoride are especially preferred. As a method of covering beforehand, a synthetic resin solvent is dissolved or distributed, and a silicon compound is mixed and kneaded in the solution. The method of grinding the solid obtained by drying the solution is preferred.

122066.A, JP.2-66856.A, The spacing indicated in each gazette, such as 2-245473, density, the carbon material of the size of microcrystal, The mixture of natural graphite and an artificial graphite given in JP.5-290844.A, JP.63-24556.A, 63-13282, 63-58763, They are a vapor-phase-epitaxy carbon material given in JP.6-212617.A, and the material by which heating calcination was carried out at the temperature over 2400 °C in difficulty graphitized carbon given in JP.5-182864.A, And material with the peak of the X diffraction equivalent to two or more 002nd page, JP.5-307957.A, 5-307958, 7-86862, the meso face carbon material compounded by the 8-315829 gazette by pitch calcination of the statement. To black lead and the pen which have an enveloping layer of a statement in JP.6-84516.A, Carbon materials, such as poly acene material containing the baking body of various kinds of granules, a microsphere, a plate-like object, microfilament, the carbon material of the shape of a whisker, phenol resin, acrylonitrile resin, and furfuryl alcohol resin and a hydrogen atom, etc. can be mentioned. As an example as a conducting agent, natural graphite, such as flaky graphite, scaly graphite, and earthy graphite, High-temperature-baking objects, such as petroleum coke, coal coks, cellulose, sugars, and a mesophase pitch, Graphite, such as artificial graphites, such as vapor-phase-epitaxy black lead, acetylene black, Carbon materials, such as carbon black, such as furnace black, Kitchen black, channel black, lamp black, and thermal black, an asphalt pitch, coal tar, activated carbon, a meso fuze pitch, and poly acene, are preferred. These may be used independently and may be used as a mixture.

[0021]In particular, the baking body of a carbon material given in JP.5-182864.A, various kinds of granules, a microsphere, a plate-like object, textiles, the carbon material of the shape of a whisker and a mesophase pitch, phenol resin, and acrylonitrile resin and the poly acene material which contains a hydrogen atom further are preferred. scaly natural graphite especially -- a mixture -- it is desirable in order to strengthen a film. 5 to 1900 % of the weight of the mixture ratio is preferred to a silicon compound. In particular, 20 to 500 % of the weight is preferred, 30 to 400 % of the weight is preferred. Although various things can be used as a mean grain size of a carbonaceous material, 0.01-50 micrometers is preferred, 0.02-30 micrometers is more preferred, and 0.05-5 micrometers is the most preferred.

[0022]As a conducting agent, other carbonaceous materials can be used as follows. When the ratio of the lithium which can carry out insertion discharge to a silicon atom is expressed with  $Li_x Si$  as a charge-and-discharge range of a silicon compound negative pole material,  $x=0-4.2$  is preferred. As a result of considering cycle-life improvement of silicon wholeheartedly, when stopped in the range of  $x=0-0.7$ , the cycle life found out improving greatly. In  $x=3.7$ , it was about 0.05V to being 1 as opposed to 1 at charging potential / a lithium metal counter electrode ] 0.0V in  $x=4.2$  including excess voltage, as opposed to the shape of a discharge curve changing and a discharge curve flat to the 0.5V (body lithium metal) neighborhood in a 0.0V charge-dinch being obtained at this time, -- more than 0.05V -- especially -- more than 0.08V ( $x=3.8$ ) -- about -- the gently-sloping curve which has average voltage in 0.4V is obtained. That is, the direction which increased charge beginning-and-the-end voltage, found out the specific phenomenon in which discharge potential fell. The phenomenon which the

reversibility of the charge-and-discharge reaction also went up was found out.

[0023] As the charge beginning-and-the-end method in this invention, although methods, such as combination of an open circuit constant voltage, a closed circuit constant voltage, current, time, and the small current charge after high current charge, are used, the method of setting up and doubling the current at the time of a closed circuit constant voltage, and setting up charging time especially, is preferred. A constant voltage value is set up in a mentioned range. As for a current value, it is preferred to stop charge, when it goes into 0.1 to 10% of range of 1 hour rate current in a constant-voltage field.

[0024] Although the method with the effect of improving a cycle life had been described separately, maintaining the high capacity of a silicon compound, the still more desirable mode found out acquiring the still higher improvement effect with the combination of a described method.

[0025] In this invention, it is combinable with the compound which can carry out insertion discharge of the lithium, such as the other carbonaceous materials of the silicon compound of this invention, an oxide material, a nitride material, sulfide material, a lithium metal, and a lithium alloy, as a negative pole material. Especially when using a transition metal oxide for a positive electrode material, it uses together with a lithium metal or a lithium alloy.

[0026] The positive electrode material used by this invention has an especially preferred lithium containing transition metal oxide, although the transition metal oxide in which the insertion discharge of the lithium can be carried out is used. It is an oxide which mainly contains preferably Ti, V, Cr, Mn, Fe, Co, nickel, Mo, at least one sort of transition metal elements chosen from W, and lithium, and the mole ratio of lithium and a transition metal is a compound of 0.3 thru/or 2.2. It is an oxide which mainly contains more preferably at least one sort of transition metal elements chosen from V, Cr, Mn, Fe, Co, and nickel, and lithium, and the mole ratio of lithium and a transition metal is a compound of 0.3 thru/or 2.2. aluminum, Ga, In, germanium, Sn, Pb, Sb, Bi, Si, P, S, etc, may be contained in less than 30 mole percents to the transition metal which mainly exists. In the above-mentioned positive active material, it is general formula  $Li_xMO_2$  (0.1  $\leq$  M=Co and 1) at least one sort of nickel, Fe, and Mn using at least one sort of material which has the Spinel structure expressed with  $x=0.1-2$  or  $Li_yN_xO_4$  (N=Mn y=0-2) -- this -- better -- "". Specifically  $Li_xCoO_2$ ,  $Li_xNiO_2$ ,  $Li_xMnO_2$ ,  $Li_xCo$  nickel,  $Li_xFe$   $Li_xCo_yV_{2-x}O_4$ ,  $Li_xCo_yFe_{2-x}O_4$ ,  $Li_xMn_yO_4$ ,  $Li_xMn_xCo_{2-x}O_4$ ,  $Li_xMn_xnickel_{2-x}O_4$ ,  $Li_xMn_yV_{2-x}O_4$ , it is  $Li_xMn_yFe_{2-x}O_4$  (it is x= 0.02-1.2, a= 0.1 to 0.9, b= 0.8 to 0.98, c= 1.6-1.96, and z= 2.01-2.3 here).

[0027] Positive active material is  $Li_yM_xO_{1-x}O_2$  (0.1  $\leq$  M=Co and 1) At least one sort of nickel, Fe, and Mn O=Co, nickel, Fe, Mn, aluminum, Zn, Cu, Mo, Ag, W, Ga, In, Sn, Pb, Sb, At least one sort other than Mn in Si, B, and P y= 0-1.2, material containing a= 0.5-1. Or  $Li_y(N_xE_{1-x})_2O_4$  (0.1  $\leq$  M=Mn E=Co and 1) nickel, Fe, Mn, aluminum, Zn, Cu, Mo, Ag, W, Ga, In, Sn, Pb, Sb, Si, S, and P E have especially a preferred thing for which at least one sort of material which has the Spinel structure expressed with 1 son be 1-0.2 z=0-2 at least is used. As most desirable lithium containing transition metal oxide,

$\text{Li}_x\text{CoO}_2$ ,  $\text{Li}_x\text{NiO}_2$ ,  $\text{Li}_x\text{MnO}_2$ ,  $\text{Li}_x\text{Co}_{1-x}\text{Ni}_x\text{O}_2$ ,  $\text{Li}_x\text{Mn}_{2-x}\text{O}_4$ , and  $\text{Li}_x\text{Co}_{1-y}\text{V}_{y/2}\text{O}_2$  ( $x=0.02\text{--}1.2$ ,  $y=0.1$  to  $0.9$ ;  $b=0.8$  to  $0.98$ ,  $z=2.01\text{--}2.3$ ) are raised. The value of  $x$  is a value before a charge-and-discharge start, and is fluctuated by charge and discharge. Although the positive active material used by this invention is compoundable by the method and solution reaction which mix a lithium compound and a transition metal compound and are calcinated, especially its calcinating method is preferred. The details for calcination are indicated to the paragraph 35 of JP, 6-60,867, A, JP, 7-14,579, A, etc., and these methods can be used for them. The positive active material obtained by calcination may be used after water, aqueous acids, an alkaline aqueous solution, and an organic solvent wash. It may be the method of compounding by making a transition metal oxide react to a lithium metal, a lithium alkyl, butyl lithium, and a transition metal oxide as a method of inserting a lithium ion chemically. [0028] Although the mean grain size in particular of the positive active material used by this invention is not limited, 0.1-50 micrometers is preferred. It is preferred that the volume of a 0.5-30-micrometer particle is not less than 25%, it is still more preferred that the volume which a particle group with a particle diameter of 3 micrometers or less occupies is 18% or less of whole product, and the volume which not less than 15-micrometer a particle group of 25 micrometers or less occupies is 18% or less of whole product. Although not limited especially as specific surface area, 0.01-50-m<sup>2</sup>/g is especially preferred at a BET adsorption method, and 0.2-m<sup>2</sup>/g-1-m<sup>2</sup>/g is preferred. As the pH of supernatant liquid when the positive active material 5g is melted in 100 ml of distilled water, 10 or less (7 or more) are preferred.

[0029] When obtaining the positive active material of this invention by calcination, it is 700-1200 °C that it is 500-1500 °C as calcination temperature desirable still more preferably, and it is 750-1000 °C especially preferably. As firing time, 4 to 30 hours is 6 to 20 hours desirable still more preferably, and it is 6 to 15 hours especially preferably.

[0030] If the conducting agent used for the mixture of this invention is a electron conductive material which does not cause a chemical change in the constituted cell, it is [ anything ] good. As an example, natural graphite, such as flaky graphite, acetylene graphite, and earthy graphite, petroleum coke, High-temperature-firing objects, such as coal corks, cellulose, sugars, and a mesophase pitch. Graphites, such as artificial graphites, such as vapor-phase-epitaxy black lead, acetylene black, Furnace black, Kishifen black, channel black, lamp black, Carbon black, such as thermal black, an asphalt pitch, coal tar, Conductive metallic oxides, such as conductive whiskers, such as metal powders, such as conductive fibers, such as carbon materials, such as activated carbon, a meso fuses pitch, and poly acene, and a metal fiber, copper, nickel, aluminum, and silver, a zinc oxide, and potassium titanate, and titanium oxide, etc. can be mentioned. It is desirable when an aspect ratio uses five or more plate-like things in black lead. In these, graphite and carbon black are preferred, as for the size of particles, 0.01 micrometers or more and 20 micrometers or less are preferred, and its particle (0.02 micrometers or more and 10 micrometers or less) is more preferred. These may be used independently and may use two or more sorts together. It is desirable when using together, and a 1-15-micrometer graphite-grains child is used together with carbon black, such as acetylene black.

As for the addition to the binder layer of a conducting agent, it is preferred that it is 1 to 50 % of the weight to a negative pole material or a positive electrode material, and it is especially preferred that it is 2 to 30 % of the weight. In carbon black or graphite, it is preferred that it is especially 3 to 20 % of the weight.

190318 In this invention, in order to hold an electrode compound, a binder is used. As an example of a binder, the polymer etc. which have polysaccharide, thermoplastics, and rubber elasticity are mentioned. As a desirable binder, starch, carboxymethyl cellulose, Cellulose, diacetyl cellulose, methyl cellulose, hydroxyethyl cellulose, Hydroxypropylcellulose, alginic acid Na, polyacrylic acid, Polyacrylic acid Na, polyvinyl phenol, polyvinyl methyl ether, Polyvinyl alcohol, a polyvinyl pyrrolidone, polyacrylamide, Water-soluble polymer, such as polyhydroxy (meta) acrylate and a styrene maleic acid copolymer, Polyvinylchloride, polytetra FLUOROCO ethylene, polyvinylidene fluoride, A tetrafluoroethylene-hexafluoropropylene copolymer, a vinylidene fluoride tetrafluoroethylene-hexafluoropropylene copolymer, Polyethylene, polypropylene, an ethylene-propylene-diene terpolymer (EPDM). The acrylic ester copolymer (meta), acrylic acid (meta) ester acrylonitrile copolymer containing acrylic ester (meta), such as sulfonation EPDM, polyvinyl-acetal resin, a methylmethacrylate, and 2-ethylhexyl acrylate, The polyvinyl ester copolymer containing vinyl ester, such as vinyl acetate, A styrene butadiene copolymer, an acrylonitrile butadiene copolymer, Polybutadiene, nitrile rubber, fluorocarbon rubber, polyethylene oxide, An emulsion (latex) or suspension, such as polyester polyurethane resin, polyether polyurethane resin, polycarbonate polyurethane resin, polyester resin, phenol resin, and an epoxy resin, can be mentioned. Latex of a polyacrylic ester system, carboxymethyl cellulose, polytetrafluoroethylene, and polyvinylidene fluoride are mentioned especially. As for these binders, it is preferred to use what distributed minute powder in water, it is more preferred to use that whose average size of the particles in dispersion liquid is 0.01-6 micrometers and it is preferred especially to use that is 0.05-1 micrometer, it can be independent, or it can mix and these binders can be used. When there are few additions of a binder, the holding power and cohesive force of an electrode compound are weak. If too large, an electrode body product will increase and electrode unit volume or the capacity per unit weight will decrease. As for the addition of a binder, 1 to 30 % of the weight is preferred for such a reason, and 2 to 10 % of the weight is especially preferred.

[0032] In the constituted cell, a bulking agent can be used anything, if it is the fibrous material which does not cause a chemical change. Usually, textiles, such as olefin system polymer, such as polypropylene and polyethylene, glass, and carbon, are used. Although the addition in particular of a filler is not limited, 0 to 30 % of the weight is preferred. The thing known as an inorganic and organic solid electrolyte can be used for an ion conducting agent, and it is indicated in the paragraph of the electrolysis solution for details. A pressure enhancement agent is a compound which increases the internal pressure of a cell, and carbonate, such as  $\text{Na}_2\text{CO}_3$ , is examples of representation.

[0033] The anodes of the charge collector which can be used by this invention are aluminum, stainless steel, nickel, titanium, or these alloys, and negative electrodes are copper, stainless steel, nickel

tinium, or these alloys. The gestalt of a charge collector is foil, an expanded metal, a punching metal, or a wire gauze. In particular, to an anode, copper foil is [ aluminium foil and a negative electrode ] preferred. As thickness of foil, 7 micrometers - 100 micrometers are 7 micrometers - 80 micrometers desirable still more preferably, and they are 7 micrometers - 20 micrometers especially preferably. As thickness of an expanded metal, a punching metal, and a wire gauze, 7 micrometers - 200 micrometers are 7 micrometers - 150 micrometers desirable still more preferably, and they are 7 micrometers - 100 micrometers especially preferably. As purity of a charge collector, not less than 98% is not less than 99% desirable still more preferably, and is not less than 99.3%, especially preferably. Acid, alkali, an organic solvent, etc. may wash the surface of a charge collector.

[0034] The thing of a charge collector in which the metal layer was formed on both sides of a plastic sheet is still more preferred in order to make thickness thin. The thing of a plastic excellent in ductility and heat resistance is preferred, for example, it is polyethylene terephthalate. Only with metal, since there is almost no elasticity, it is weak to external force. If a metal layer is formed on a plastic, it will become strong against a shock. More specifically, a charge collector may be a compound charge collector which covered substrates, such as a synthetic resin film and paper, with the substances of electron conductivity. As a synthetic resin film used as a substrate, a fluoro-resin, polyethylene terephthalate, polycarbonate, polyvinyl chloride, polystyrene, polyethylene, polypropylene, polyimide, polyamide, a cellulose dielectric, and polysulfone can be mentioned. As a substance of the electron conductivity which covers a substrate, metallic elements and these alloys, such as carbonaceous materials, such as black lead and carbon black, aluminum, copper, nickel, chromium, iron, molybdenum, gold, and silver, can be mentioned. Especially the substance of desirable electron conductivity is metal, and are aluminum, copper, nickel, and stainless steel. A compound charge collector may be a gestalt which pastes the sheet and metal sheet of a substrate together, and may form a metal layer by vacuum evaporation etc.

[0035] Next, the composition of the positive/negative electrode in this invention is explained. As for a positive/negative electrode, it is preferred that it is the gestalt which applied the electrode compound to both sides of a charge collector. In this case, even if the number of layers per one side is one layer, it may comprise more than two-layer. When the number of the layers per one side is two or more, a positive-active-material (or negative pole material) contained layer may be more than two-layer. More desirable composition is a case where it comprises a layer containing positive active material (or negative pole material), and a layer which does not contain positive active material (or negative pole material). In the layer which does not contain positive active material (or negative pole material), The protective layer for protecting the layer containing positive active material (or negative pole material), The interlayer between the divided positive-active-material (or negative pole material) contained layers, the under coat between a positive-active-material (or negative pole material) contained layer and a charge collector, etc. are, and these are named generically in this invention and it is called an auxiliary layer.

[0036] As for a protective layer, it is preferred that it is in either both positive/negative electrodes or a

positive/negative electrode, in a negative electrode, as for a negative electrode, when inserting lithium in a negative pole material within a cell, it is desirable that it is a gestalt which has a protective layer. A protective layer consists of at least one layer, and may be constituted by one or two or more layers of a different kind. It may be a gestalt which has a protective layer only on one side of the binder layers of both sides of a charge collector. These protective layers comprise particles, a binder, etc. of insoluble in water nature. The binder used when forming the above-mentioned electrode compound can be used for a binder. As particles of insoluble in water nature, a various conductive particle and the organic and inorganic particles which do not have conductivity substantially can be used. 100 PPM or less and the desirable insoluble thing of the solubility to the water of insoluble in water nature particles are preferred. As for the rate of the particles contained in a protective layer, 2.5 % of the weight or more and 96 % of the weight or less are preferred, it is more preferred, and is preferred, [ of 10 % of the weight or more and especially 93 % of the weight or less ] [ of 5 % of the weight or more and 95 % of the weight or less ]

[0037] As a conductive particle of insoluble in water nature, carbon particles, such as metal, a metallic oxide, a metal fiber, carbon fiber, carbon black, and black lead, can be mentioned. In these water-insoluble conductive particles, what has low reactivity with an alkaline metal, especially lithium is preferred, and metal powder and a carbon particle are more preferred. As electrical resistivity at 20 °C of the element which constitutes particles, below  $5 \times 10^{-9}$  omega-m is preferred.

[0038] As metal powder, metal with low reactivity with lithium, i.e., the metal which cannot make a lithium alloy easily, is preferred, and, specifically, copper, nickel, iron, chromium, molybdenum, titanium, tungsten, and tantalum are preferred. A needle and a column, tubular, and massive any may be sufficient as the form of such metal powder, 0.02 micrometers or more and 20 micrometers or less have a preferred overall diameter, and it is more preferred [ of 0.1 micrometers or more and 10 micrometers or less ]. That [ pair ] in which the surface has not oxidized too much is preferred, and as for such metal powder, when having oxidized, heat-treating by reducing atmosphere is preferred.

[0039] As a carbon particle, the publicly known carbon material used as an electrical conducting material used together when an electrode active material is not conductivity conventionally can be used. The conducting agent used when specifically making an electrode compound is used.

[0040] As insoluble in water nature particles which do not have conductivity substantially, the impalpable powder of Teflon, SiC, aluminum nitride, alumina, zirconia, magnesia, mullite, forsterite, and a steatite can be mentioned. When these particles may be used together with a conductive particle and used by 0.01 or more times of a conductive particle, and 10 or less times, they are preferred.

[0041] A positive (negative) electrode sheet can be created by applying, drying and compressing the mixture of a right (negative) pole on a charge collector. Preparation of a mixture mixes positive active material (or negative pole material) and a conducting agent. A binder (the suspension of resin powder or emulsion-like thing) and carrier fluid can be added, kneading mixing can be carried out, and it can carry out successingly by stirring mixers, such as a mixer, a homogenizer, dissolver, a planetary

mixer, a paint shaker, and a sand mill, and a dispersion machine distributing. Water is preferred although water or an organic solvent is used as carrier fluid. In addition, additive agents, such as a bulking agent, an ion conducting agent, and a pressure enhancement agent, may be added suitably. As for the pH of dispersion liquid, in a negative electrode, 7-12 are preferred at 5-10, and an anode, [0042] Although spreading can be performed by various methods, the reverse roll method, the Dallech-bawl method, the braid method, the knife method, the extrusion method, a slide agglomeration test, the curtain method, the photogravure method, the bar method, a dip method, and the squeeze method, can be mentioned, for example. The method of using an extrusion die, and especially the method of using a slide casting machine are preferred. As for spreading, it is preferred to carry out the speed for 0.1-100-mm. Under the present circumstances, according to the liquid nature of mixture paste, and drying property, the surface state of a good coating layer can be acquired by selecting the above-mentioned coating method. It is preferred from viewpoints of manufacture of a uniform electrode, a manufacturing cost, etc. to apply two or more of these layers simultaneously, when electrode layers are two or more layers. The thickness, length, and width of the coating layer are decided with the size of a cell. The thickness of a typical coating layer is 10-1000 micrometers in the state where it was compressed after desiccation. The electrode sheet after spreading is dried and dried by the hot wind, a vacuum, infrared rays, far-infrared rays, an electron beam, and the operation of the clamp style. These methods can be independent, or can be combined and can be used. The range of drying temperature of 80-350 °C is preferred, and its range which is 100-260 °C is especially preferred. As for the water content after desiccation, 2000 ppm or less are preferred, and its 500 ppm or less are more preferred. Although the compression of an electrode sheet can use the pressing method generally adopted, a die-press method and the calendar pressing method are especially preferred. Although press pressure in particular is not limited, 10 kg/cm<sup>2</sup> - 300 kg/cm<sup>2</sup> are preferred. As for the pressing speed of the calendar pressing method, the amount of 0.1-50-mm is desirable. Room temperature -200 °C of press temperature is preferred.

[0043] The separator which can be used by this invention has the large degree of ion permeation, to have a predetermined mechanical strength, and what is necessary is just an insulating thin film, and as construction material, Ciefin system polymer, fluorine system polymer, cellulose type polymer, polyimide, nylon, glass fiber, and an alumina fiber are used, and a nonwoven fabric, textile fabrics, and a microporous film are used as a geotextile. In particular, as construction material, the mixture of polypropylene, polyethylene, polypropylene, the mixture of polyethylene and polypropylene, and Teflon and the mixture of polyethylene and Teflon are preferred, and what is a microporous film as a geotextile is preferred. In particular, the 5-50-micrometer-thick microporous film whose aperture is 0.01-1 micrometer is preferred. Even if these microporous films are independent films, they may be complex films which consist of more than two-layer [ from which character, such as shape, density etc. of a fine hole, and construction material, differs ]. For example, the complex film which pasted the polyethylene film and the polypropylene film together can be mentioned.

[0044] Generally an electrolysis solution comprises a supporting electrolyte and a solvent. As for the

supporting electrolyte in a lithium secondary battery, lithium salt is mainly used. As lithium salt which can be used by this invention, for example  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiPF}_4$ ,  $\text{LiClO}_4\text{CO}_2$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiB}_6\text{Cl}_{10}$ . The fluorosulfonic acid expressed with  $\text{F}_{2n}$  of  $\text{LiSO}_2\text{C}_{2n+1}$  ( $n$  is six or less positive integer), the imide salt ( $m$ ) expressed with  $\text{LiN}(\text{SO}_2\text{C}_{2m+1})(\text{SO}_2\text{C}_{2m+1})$  the methide salt ( $p$ ) as which  $n$  is expressed in six or less positive integer and  $\text{LiC}(\text{SO}_2\text{C}_{2p+1})(\text{SO}_2\text{C}_{2p+1})(\text{SO}_2\text{C}_{2p+1})$ , respectively  $q$  and  $r$ , respectively six or less positive integer, low-grade aliphatic-carboxylic-acid lithium, Li salt, such as  $\text{LiAlCl}_4$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{LiI}$ , chloraborane-lithium, and 4 phenyl lithium borate, can be raised, and these kinds or two sorts or more can be mixed and used. What dissolved  $\text{LiPF}_6$  and/or  $\text{LiPF}_4$  especially is preferred. Although the concentration in particular of a supporting electrolyte is not limited, its 0.2-3 mol per l. of electrolysis solution is preferred.

[0045] As a solvent which can be used by this invention, propylene carbonate, ethylene carbonate, Butylene carbonate, chloroethylene carbonate, and trifluoromethyl ethylene carbonate, Difluoromethyl ethylene carbonate and monofluoromethyl ethylene carbonate, Methyl hexafluoride acetate, methyl trifluoride acetate, Dimethyl carbonate, Diethyl carbonate, methyl ethyl carbonate, gamma-butyrolactone, Methyl formate, methyl acetate, 1,2-dimethoxyethane, a tetrahydrofuran, 2-methyltetrahydrofuran, dimethyl sulfoxide, 1,3-dioxolane, 2,2-bis(trifluoromethyl)-1,3-dioxolane, a formamide, Dimethylformamide, dioxolane, dioxane, acetonitrile, Nitromethane, ethylmono-glyme, trialkyl phosphate, boric acid triester, Trimethoxy methane, a dioxolane derivative, sulfolane, 3-methyl-2-oxazolidinone,  $\beta$ -alkyl sydnone (alkyl groups are propyl, isopropyl, a butyl group, etc.), a propylene carbonate derivative, a tetrahydrofuran derivative, ethyl ether, Aprotic organic solvents, such as 1,3-propanes Soltol, can be mentioned, and these kinds or two sorts or more are mixed and used. In these, the solvent of a carbonate system is preferred and it is preferred especially to mix and use cyclic carbonate and non-cyclic carbonate. As cyclic carbonates, ethylene carbonate and propylene carbonate are preferred. As non-cyclic carbonate, diethyl carbonate, dimethyl carbonate, and MECHIRUUECHIRUKABONETO \*\* are preferred. As an electrolysis solution which can be used by this invention, ethylene carbonate, propylene carbonate, The electrolysis solution which contains  $\text{LiClO}_4\text{SO}_3$ ,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ , and/or  $\text{LiPF}_6$  in the electrolysis solution which mixed suitably 1,2-dimethoxyethane, dimethyl carbonate, or diethyl carbonate is preferred. Especially to at least one mixed solvent of propylene carbonate, at least one side of ethylene carbonate and dimethyl carbonate, or diethyl carbonate. A kind of salt selected from  $\text{LiClO}_4\text{SO}_3$ ,  $\text{LiClO}_4$ , or  $\text{LiBF}_4$  and the electrolysis solution containing  $\text{LiPF}_6$  are preferred at least. The quantity in particular that adds these electrolytes solutions in a cell is not limited, but can be used according to the quantity of a positive electrode material or a negative pole material, or the size of a cell.

[0046] The following solid electrolytes can also be used together besides an electrolysis solution. It is divided into an inorganic solid electrolyte and an organic solid electrolyte as a solid electrolyte. The

nitrides of Li, the halogenide, the oxygen acid salt, etc. are well known by the inorganic solid electrolyte. Li<sub>3</sub>N, Li<sub>2</sub>, Li<sub>2</sub>Ni<sub>2</sub> especially, Li<sub>3</sub>N-Li<sub>2</sub>-LiOH, Li<sub>4</sub>SiO<sub>4</sub>, Li<sub>2</sub>SiO<sub>4</sub>-Li<sub>2</sub>-LiOH, xLi<sub>2</sub>PO<sub>4</sub>-(1-x); Li<sub>2</sub>SiO<sub>4</sub>, Li<sub>2</sub>SiS<sub>2</sub>, a phosphorus sulfide compound, etc. are effective.

[0047] The polymer which contains a polyethylene oxide derivative or this derivative in an organic solid electrolyte, The polymers matrix material which made polymer containing a polypropylene oxide derivative or this derivative, polymer containing an ionic dissociation group, polymer containing an ionic dissociation group, the mixture of the above-mentioned aprotic electrolysis solution and phosphoric ester polymer, and an aprotic polar solvent contain is effective. There is also the method of adding polyacrylonitrile to an electrolysis solution. How to use together inorganic matter and an organic solid electrolyte is also known.

[0048] Other compounds may be added to an electrolyte in order to improve discharge and a charging and discharging characteristic. For example, pyridine, pyrrolines, pyrrols, a triphenylamine, phenylcarbazole, Triethyl phosphite, triethanolamine, cyclic ether, Ethylenediamine, n-glyme, hexalin acid TORIAMIDO, a nitrobenzene derivative, Sulfur, a quinonimine dye, N-substitution oxazolidinone, and N and N'-substitution imidazolidinone, Ethylene glycol dialkyl ether, quaternary ammonium salt, a polyethylene glycol, Pyrrole, 2-methoxyethanol, AlCl<sub>3</sub>, the monomer of a conductive polymer electrode active material, The triethylene phosphoramido, trialkylphosphine, morpholine, The crown ether like an aryl compound and the 12-crown-4 and hexamethylphosphoric triamide with a carbonyl group, 4-alkyl morpholines, the bicyclic third class amine, oil, the fourth class phosphonium salt, the third class sulfonium salt, etc. can be mentioned. Especially a desirable thing is a case where it was independent, or combined and it uses, about a triphenylamine and phenylcarbazole.

[0049] In order to make an electrolysis solution into incombustibility, a halogen-containing solvent, for example, a carbon tetrachloride, and 3 fluoridation ethylene chloride can be included in an electrolysis solution. In order to give fitness to high temperature preservation, carbon dioxide can be included in an electrolysis solution.

[0050] As for an electrolysis solution, it is desirable not to contain a part for moisture and free acid as much as possible. For this reason, as for the raw material of an electrolysis solution, what carried out sufficient drying and refining is preferred. Adjustment of an electrolysis solution has { the inside of dry air not more than minus 30 °C or inactive gas } the preferred dew point, 0.1-500 ppm of quantity for the moisture in an electrolysis solution and free acid is 0.2-100 ppm more preferably.

[0051] Although an electrolysis solution may pour in the whole quantity at once, it is preferred to pour in in 2 steps or more. When pouring in in 2 steps or more, the presentation (after pouring in the solution which dissolved lithium salt in the nonaqueous solvent or the nonaqueous solvent, the solution which dissolved lithium salt in the nonaqueous solvent or nonaqueous solvent whose viscosity is higher than said solvent is poured in) which is different also by the same presentation may be sufficient as each liquid. It may perform decompressing a battery can for shortening of the injection time of an electrolysis solution, etc., or applying a centrifugal force and an ultrasonic wave to a battery

can.

[0052] The steel board with which the battery can and battery lid which can be used by this invention performed the nickel plate as construction material, a stainless steel plate (SUS304, SUS304L, and SUS304N.) It is SUS316, SUS316L, SUS430, SUS444 grade, the stainless steel plate (same as the above) that performed the nickel plate, aluminum or its alloy, nickel, titanium, and copper, and is round shape tubed, ellipse form tubed one, square tubed, and rectangle tubed as shape. Especially when an armor can serves as a negative pole terminal, a stainless steel plate and the steel board which performed the nickel plate are preferred, and when an armor can serves as a positive pole terminal, a stainless steel plate, aluminum, or its alloy is preferred. Any, such as a button, coin, a sheet, a cylinder, and an angle, may be sufficient as the shape of a battery can. A safety valve can be used for an oxidation board as a measure against the internal pressure rise of a battery can. In addition, the method of putting in sitting can also be used for members, such as a battery can and a gasket. In addition, it may be equipped with various safety elements (a fuse, bimetal, a PTC element, etc. as [ For example, ] an overcurrent-protection element known from the former.

[0053] Metal (for example, iron, nickel, titanium, chromium, molybdenum, copper, aluminum, etc.) with electrical conductivity and those alloys can be used for the lead board used by this invention. A publicly known method (electric welding of an example, a direct current, or exchange, laser welding, ultrasonic welding) can be used for the welding process of a battery lid, a battery can, an electrode sheet, and a lead board. The compound and mixture which are known from the former, such as asphalt, can be used for the sealing compound for obturation.

[0054] As construction material, they are olefin system polymer, fluorine system polymer, cellulose type polymer, polyimide, and polyamide, from organic solvent-proof nature and low-water-flow part permeability, the gasket which can be used by this invention has preferred olefin system polymer, and especially its polymer of a propylene subject is preferred. It is preferred that it is block copolymerization polymer of propylene and ethylene.

[0055] As for the cell assembled as mentioned above, it is preferred to perform aging processing. There are pretreatment, activation, post-processing, etc. in aging processing, and the cell which was excellent in high charge-and-discharge capacity and cycle nature by this can be manufactured. Pretreatment is processing for equalizing distribution of lithium in an electrode, and arbitrary combination of the temperature control for making dissolution control of lithium and distribution of lithium uniform, rocking and/or a rotating process, and charge and discharge is performed, for example. Activation is processing for making lithium insert to the negative electrode of a cell proper, and it is preferred to insert 50 to 120% of the lithium insertion amount of the time of actual use charge of a cell. Post-processing is processing for fully carrying out activation, has this [ for a judgment / charge-and-discharge processing ], and can be arbitrarily combined with the storage processing for making a cell reaction uniform.

[0056] The desirable aging conditions (pretreatment conditions) before activation of this invention are as follows. The temperature of not less than 30 °C 70 °C or less is preferred, is more preferred, and is

still more preferred, { of not less than 40 °C 60 °C or less } { of not less than 30 °C 60 °C or less } As for open circuit voltage, less than more than 2.5V3.8V is preferred, less than more than 2.5V3.5V is more preferred, and less than more than 2.8V3.3V is still more preferred. As for an aging period, 20 or less days will be preferred the 1st day or more, and especially its 15 or less days will be preferred the 1st day or more. As for the charge voltages of activation, more than 4.0V is preferred, less than more than 4.0V4.2V is more preferred, and less than more than 4.1V4.2V is still more preferred. As aging conditions after activation, less than more than 3.9V4.3V has preferred open circuit voltage, less than more than 4.0V4.2V especially is preferred, and the temperature of not less than 30 °C 70 °C or less is preferred, and is preferred. { of not less than 40 °C especially 60 °C or less } As for an aging period, 20 or less days will be preferred the 0.2nd day or more, and especially its five or less days will be preferred the 0.5th day or more.

[0057] The cell of this invention is covered with a sheathing material if needed. As a sheathing material, there are heat-shrinkable tubing, adhesive tape, a metallic film, paper, cloth, a paint, a plastic case, etc. The portion of the exterior discolored with heat in part at least is provided, and it may be made for a heat history in use to be known.

[0058] The cell of this invention constructs two or more in series and/or in parallel if needed, and is stored by the battery pack. A safety circuit (circuit with the function which intercepts current if the voltage of each cell and/or the whole cell group, temperature, current, etc. are monitored and it is required) besides safety elements, such as a high temperature coefficient resistor, a thermal cutout, a fuse, and/or a current cutoff element, may be established in a battery pack. The anode of each cell and a negative pole terminal, the whole cell group and the temperature detection terminals of each cell, the current detection terminal of the whole cell group, etc. can also be provided in a battery pack, as an external terminal in addition to the anode and negative pole terminal of the whole cell group. Voltage conversion circuits (DC-DC converter etc.) may be built in a battery pack. It may fix by welding a lead board, and connection of each cell may be fixed so that it can detach and attach easily with a socket etc. Display functions, such as battery remaining capacity, existence of charge, and a use count, may be provided in a battery pack.

[0059] The cell of this invention is used for various apparatus. Especially A video movie, a portable videocassette recorder with a built-in monitor, a movie camera with a built-in monitor, it is preferred to be used for a digital camera, a compact camera, a single-lens reflex camera, a disposable camera, a notebook-sized personal computer, a note type word processor, an electronic notebook, a cellular phone, a cordless telephone, a mustached camber, a power tool, an electric mixer, a car, etc.

[0060]

[Example] Although an example is raised to below and this invention is explained in more detail, this invention is not limited to an example.

[0061] As example-1 negative pole material, as a polycrystal silicon simple substance (compound-1) and an alloy compound of the following compounded metallurgically, Si-Ag alloy (compound-2 [Atomic ratio 30-70] the atomic ratio 60-40 and compound-3 the atomic ratio 80-20 and compound-

4). Si-aluminum compound-5 atomic ratio 60-40), Si-Ag-Cd (compound-6 60-30-10), Si-In (compound-7 atomic ratio 60-40), Si-Au (compound-8 8 atomic ratio 60-40), Si-Ag-In (compound-9 atomic ratio 60-30-10), Si-germanium (compound-10 atomic ratio 60-40), Si-Ag-Sn (compound-11 atomic ratio 60-30-10), Si-Ag-Bb (compound-12 atomic ratio 60-30-10). The silicon produced from Si-Ag-nickel (compound-13 atomic ratio 60-30-10) and Li<sub>2</sub>Si compounded metallurgically by grinding the silicon which made to diluted 100% using isopropyl alcohol in argon gas (compound-14), Si-SiO<sub>2</sub> (the compound-15 weight ratio 80-20) which used as the granular material the solid produced by mixing silicon and colloidal silica of compound-1 and heating at 1000 °C in the vibration mill in argon gas. Compound-16 The weight ratio 90-10 and compound-17 Weight ratio 60-40 Si-aluminum<sub>2</sub>O<sub>3</sub> obtained using alumina sol in the similar way (compound-18 weight ratio 90-10). As the compound (compound-19 compound-6-SiO<sub>2</sub> weight ratio 90-10) to which SiO<sub>2</sub> was made to adhere by the method same to compound-2 as compound-18, and a compound plated with the nonelectrolytic plating method to the silicon surface of compound-1. The silicon (as dextrin and a source of Ag, it is AgNO<sub>3</sub> as a reducing agent (atomic ratio 60-40 of compound-20 Si-Ag) which carried out Ag plating. Similarly nickel plating was carried out (as a reducing agent, it NaBH<sub>4</sub>-PbO<sub>2</sub> and). As a source of nickel, NiSC<sub>2</sub> silicon (atomic ratio 60-40 of compound-21 Si-nickel, the compound-22 atomic ratio 80-20, and compound-23 atomic ratio 30-70). The silicon (ZnO as NaBH<sub>4</sub> and a source of Zn as a reducing agent) (atomic ratio 60-40 of compound-24 Si-Zn) which similarly carried out Zn plating. It dries, after 30g's adding in the liquid which melted the compound (compound-25 compound-2-nickel weight ratio 80-20) polyvinylidene fluoride 3g which plated nickel with the electroless deposition method for compound-2 in 50 g of N-methyl pyrrolidone and carrying out the mix of the silicon of compound-1 to it. The granular material (compound-26) ground with the automatic mortar was used. The compound which covered polyvinylidene fluoride with the described method for compound-2 (compound-27 weight ratio 80-10 of compound-2-polyvinylidene fluoride). The compound which furthermore covered Ag with the nonelectrolytic plating method for compound-14 (atomic ratio 60-40 of compound-28 Si-Ag). The compound which similarly covered nickel (atomic ratio 60-40 of compound-29 Si-nickel). The compound which covered polyvinylidene fluoride with the same method as compound-30 for compound-14 (compound-30 Si-polyvinylidene fluoride weight ratio 90-10). The compound which covered nickel with the nonelectrolytic plating method to compound-30 (compound-31 compound-30-nickel weight ratio 70-30). The compound which covered Ag with the nonelectrolytic plating method for compound-16 (compound-32 wt. ratio 70-30 of compound-15-Ag). The compound (compound-33 wt. ratio 70-30 of compound-15-nickel) which similarly covered nickel, and the compound (weight ratio 80-10 of compound-34 compound-15-polyvinylidene fluoride) similarly covered with polyvinylidene fluoride using compound-15 were used. The compound (compound-35 compound-34-Ag weight ratio 80-20) which covered Ag with the electroless deposition method for compound-34, the compound which similarly carried out nickel plating (compound-36 compound-34-

nickel weight ratio 80:20)

Each mean grain size of the above-mentioned negative pole material (compounds 1-36) used the particles of the range of 0.05-4 micrometers. Next, it is N-methyl-2-pyrrolidone about 10 g of poly  $\gamma$ -iod vinylidene considering the granular material produced by fully mixing scaly natural graphite of same weight with the above-mentioned negative pole material (compounds 1-36) as 130 g and a binder, it distributed to 500 ml and the negative-electrode paste was created.

[0062] 5 g of poly  $\gamma$ -iod vinylidene is continuously mixed 200 g and 10 g of acetylene black with a homogenizer and mixed as a binder in positive-active-material LiCoO<sub>2</sub>, and it is N-methyl-2-pyrrolidone, 500 ml was added, kneading mixing was carried out, and the positive electrode mixture paste was created.

[0063] Compression molding of the positive electrode mixture paste created above was carried out to both sides of the 30-micrometer-thick aluminium foil charge collector with the roller press machine after spreading and 150 °C desiccation by the braid coating machine, it judged in the predetermined size, and the band-like positive electrode sheet was created. Furthermore, drying desiccation was enough carried out with the far infrared heater all over the dry box (dew point: dry air not more than -50 °C), and the positive electrode sheet was created. Similarly, the negative electrode mixture paste was applied to a 30-micrometer copper foil charge collector, and the negative electrode sheet was created by the same method as the above-mentioned positive electrode sheet creation. The coverage of positive and negative poles adjusted the coverage of each electrode compound so that the charging capacity of the 1st cycle from which the charging capacity of the 1st cycle from which positive active material is set to 4.2V to a lithium metal, and the above-mentioned negative pole material are set to 0.6V might suit.

[0064] Next, the electrolysis solution was created as follows. By argon atmosphere, 85.3 g of diethyl carbonate was put into the polypropylene container of a 200-cc thin mouth, and 22.2 g of ethylene carbonate (a little) was dissolved every, taking care that solution temperature does not exceed 30 °C to this. Next, it dissolved in the above-mentioned polypropylene container every in small quantities in order, respectively, being careful of 0.4 g LiPF<sub>6</sub> and 12.1-g LiPF<sub>6</sub> for solution temperature not to exceed 30 °C. The obtained electrolysis solution was a water-white fluid by specific gravity 1.136. The amount of 1/10 ppm (it measures with a product made from Kyoto Electron trade name MKC-210 type CorrPhi Shari water measurement device; and 1/ free acid of moisture was 24 ppm (the bromthymol blue is used as an indicator, and using a decimolar NaOH aqueous solution, a neutralization titration is carried out and it measures).

[0065] The cylinder cell was created as follows. How to make a cell according to drawing 1 is explained. The separator was laminated to the positive electrode sheet, the separator made from a microporous polyethylene film, and negative electrode sheet part which were created above in order, and this was spirally wound around them. It stored to the iron closed-end cylindrical battery can (1) which performed nickel plating which serves this wound electrode group (2) as a negative pole terminal, and the top electric insulating plate (3) was inserted further, what laminated a positive pole

terminal (6), the insulating ring, the PTC element (63), the current cutoff object (62), and the pressure induction valve element (61) after pouring in the above-mentioned electrolysis solution into this battery can -- a gasket (5) -- passing -- the cylindrical cell was created in total.